

# Manifestation of Random First Order Transition theory in Wigner glasses

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## Abstract

We use Brownian dynamics simulations of a binary mixture of highly charged spherical colloidal particles to illustrate many of the implications of the Random First Order Transition (RFOT) theory (Phys. Rev. A. **40** 1045 (1989)), which is the only theory that provides a unified description of both the statics and dynamics of the liquid to glass transition. In accord with the RFOT predictions, we find that as the volume fraction of the colloidal particles  $\phi$ , the natural variable that controls glass formation in colloidal systems, approaches  $\phi_A$  there is an effective ergodic to non-ergodic dynamical transition, which is signaled by a dramatic slowing down of diffusion with the translational constant decaying as a power law as  $\phi \rightarrow \phi_A^-$ . In addition, using the energy metric (a measure to probe ergodicity breaking in classical many body systems) we show that the system becomes non-ergodic as  $\phi_A$  is approached. The time  $t^*$ , at which the four-point dynamical susceptibility achieves a maximum, also diverges as a power law near  $\phi_A$ . Remarkably, three independent measures of dynamics (translational diffusion coefficients, ergodic diffusion coefficient, as well  $t^*$ ) all signal that at  $\phi_A \approx 0.01$  ergodicity is broken. The translation diffusion constant, the ergodic diffusion constant, and  $(t^*)^{-1}$  all vanish as  $(\phi_A - \phi)^\gamma$  with both  $\phi_A$  and  $\gamma$  being the roughly the same for all three quantities. Below  $\phi_A$  transport involves crossing suitable free energy barriers. In this regime, the density-density correlation function decays as a stretched exponential ( $\exp(-\frac{t}{\tau_\alpha})^\beta$ ) with  $\beta \approx 0.6$ . The  $\phi$ -dependence of the relaxation time  $\tau_\alpha$  is well fit using the Vogel-Fulcher-Tamman law with the ideal glass transition occurring at  $\phi_K \approx 0.47$ . By using an approximate measure of the local entropy ( $s_3$ ) we show that below  $\phi_A$  the law of large numbers, which states that the distribution of  $s_3$  for a large subsample should be identical to the whole sample, is violated. The variations in statistical properties of observables between subsample to subsample results in dynamical heterogeneity, which we show is a consequence of violation of law of large numbers. The comprehensive analyses provided here for Wigner glass forming charged colloidal suspensions fully validate the concepts of RFOT theory.

## I. INTRODUCTION

The liquid to glass transition is subject of great interest because concepts developed in the studies of the structural glass transition (SGT) manifest themselves in other areas in condensed matter physics and biology. A growing number of experimental, theoretical, and simulation studies have established that the Random First-Order Transition (RFOT) [1] is the most viable theory of the SGT currently available. An early review can be found in [2], and a number of recent reviews have provided further analyses, limitations, and applications of RFOT [3–7]. The RFOT theory, which explains most of the universal aspects of glass forming materials, was initially inspired by exact solutions of the statics and dynamics of certain infinite ranged or mean-field spin glass models [8–12]. In the spin glass (SG) models, randomness is explicitly introduced in the Hamiltonian by assuming that the interactions between the spins are randomly distributed.

In a subsequent study, Kirkpatrick and Thirumalai [13] (KT) explicitly showed that the same general scenario also emerges using equilibrium and dynamical solutions of regular density functional Hamiltonian (DFH), appropriate for liquids, thus explaining how randomness is self-generated as a liquid undergoes SGT. Here, KT also introduced the idea or technique of inserting an infinitesimal replica symmetry breaking field into non-random Hamiltonians so that the multiplicity of states in these systems could be investigated. The study in [13] was the first paper to show that the ideas that were developed to make precise connections between statics and dynamics in SG models, which appeared to be restricted to systems with quenched disorder, could be used in any system where there are many statistically distributed metastable states. The crucial discovery in KT is that below the dynamical transition temperature,  $T_A$ , there are an extensive number,  $e^{\alpha N}$  ( $N$  is the number of particles and  $\alpha > 0$ ) of states; the liquid becomes trapped in one of the large number of metastable states. This finding allowed us to produce a consistent static and dynamical theory of the SGT across the entire temperature range using a DFH, which is known to be a reasonable starting point for describing the liquid state. Indeed, others have also judiciously exploited the observation that the dynamical transition in these systems can be described using equilibrium theories [14, 15]. At a lower temperature,  $T_K$  ( $< T_A$ ), the number of such states becomes non-extensive, and hence the entropy associated with the number of states vanishes signaling the ideal SGT. The RFOT theory has been subsequently

elaborated and expanded on by numerous authors (see for example [3, 5, 6, 16–18] and references therein) in an effort to explain glassy states of model systems. It is worth emphasizing *en passant* that in more recent discussions of RFOT only activated processes leading to transport below  $T_A$  are emphasized. Such discussions have created an erroneous impression that RFOT is largely a thermodynamic theory whereas the essence of RFOT is to cover the equilibrium and dynamical aspects above and below  $T_A$  in a consistent manner. Finally, it is worth noting that RFOT is qualitatively different from the predictions where the SGT is a regular first order phase transition [19].

Within a mean field picture the barriers separating the multiplicity of disjoint states that exist between  $T_K$  and  $T_A$  increases with the system size so that at the  $T = T_A^+$  there is a genuine ergodic to non-ergodic transition. In systems containing particles interacting via short range interactions we still expect that for  $T < T_A$  there will be finite domains with properties similar to the global metastable states predicted by mean-field theory, except that these states are no longer truly disjoint. In this case, ergodicity is effectively broken because the observation time scale,  $\tau_{obs}$  is less than the relaxation time scales, a notion that can only be understood using a consistent static and dynamical approach. The long time dynamics below  $T_A$  would then be governed by activated transport, as the domains change from one metastable state to another. Within RFOT the driving force for transport is purely entropic as the system can access a large number of states by making transitions between the so-called mosaic states [1]. The exponentially large relaxation times in glasses are most naturally obtained by considering activated transitions between different mosaic states. Very general arguments [1] lead to the conclusion that these droplets are characterized by a (diverging) length scale  $\xi \sim r^{-\frac{2}{d}}$  and a characteristic free energy barrier  $\Delta F^\ddagger \sim \xi^{\frac{d}{2}}$  where  $r = \frac{(T-T_K)}{T_K}$ , separating two adjacent mosaic states. In three dimensions, in which the present simulations are carried out,  $\xi \sim r^{-\frac{2}{3}}$  and  $\Delta F^\ddagger \sim \xi^{\frac{3}{2}}$ . Finally, because there is a distribution of relaxation times associated with the various mosaic states we expect that relaxation of various quantities, such as the density-density time correlation function, would exhibit a stretched exponential decay, which we demonstrate here for colloidal glasses.

A number of unique features emerge when a glass is pictured as being partitioned into mosaic states as  $T = T_A^+$  whose characteristic temperature-dependent size is denoted by  $\xi_i(T)$ . For the purposes of discussion we do not consider variations in the sizes of the glassy clusters. (1) Within

each mosaic state structural rearrangements can be rapid but global relaxation requires activated transitions, involving nucleation of new domains. Slow structural fluctuations in glasses occurs because of entropic driving forces that enable creation and formation of new glassy clusters by fluctuation effects. The effects of fluctuations on a system undergoing random first order transition are best characterized as  $T \rightarrow T_A^+$  using four-point susceptibility, which was first theoretically discussed by Kirkpatrick and Thirumalai [19] to differentiate between regular first order transition and RFOT, and subsequently used by many [20, 21] mostly without attribution to the original paper. (2) As the degree of supercooling increases not only does  $\xi_i(T)$  grow but also the relaxation time associated with particles that cross domain boundaries exceeds  $\tau_{obs}$ , thus leading to broken ergodicity. These physical considerations that are embedded in the droplet picture of the RFOT [1] also lead to violation of law of large numbers as the STG occurs [22].

In this paper, we illustrate some of the RFOT concepts described above using Brownian dynamics simulations of binary mixtures of charged colloidal suspensions, whose phase behavior is extremely rich and interesting on its own. Although considerable amount of work has been done to illustrate the phases of monodisperse colloidal particles much less is known about binary mixtures of charged micron-sized particles, which readily form the so called Wigner glasses. These fascinating systems form Wigner glasses with finite rigidity, as demonstrated in a pioneering study by Lindsay and Chaikin [23]. Subsequent molecular dynamics simulations confirmed that these low-density systems form Wigner glasses with ease, and could also form BCC-like substitutional crystals [24]. The ease of glass formation in these systems were further characterized in terms of localized soft modes to describe the nature of activated transport [24]. Similar ideas been used in the context of hard sphere glasses [25]. More recently, there has been renewed interest in the study of charged suspensions [26, 27] which apparently manifest (with some differences) many aspects of the SGT, revealed in simulations of binary mixtures of soft sphere systems [28–32], mixtures of Lennard Jones particles [28, 33] with additive diameter and non-additive diameter [34], and possibly even in hard sphere colloidal suspensions [35]. The advantage of studying charged suspensions containing micron-sized particles is that, in principle, video microscopy can be used to directly image the trajectories of the particles as a function of the volume fraction,  $\phi$ , thus making it possible to validate some of the predictions made in this work.

## II. METHODS

**Model.** Following our previous work [24], we simulated a binary mixture of charged colloidal suspensions, which form Wigner glasses [23]. The systems consist of  $N_1$  colloidal particles with radius  $a_1$  and  $N_2$  particles with radius  $a_2$ . The interaction potential between the colloidal particles is modeled by Derjaguin-Landau-Verwey-Overbeek (DLVO) potential, which is known to describe the interactions between highly charged micron size particles in water [36–40]. The functional form of the DLVO potential used in our simulations is,

$$V_{ij}(r_{ij}) = \frac{e^2 Z_i Z_j}{\epsilon} \left( \frac{\exp[qa_i]}{1 + qa_i} \right) \left( \frac{\exp[qa_j]}{1 + qa_j} \right) \frac{\exp[-qr_{ij}]}{r} \quad (1)$$

where  $Z_i e$  is the charge of the macroparticle  $i$ ,  $q^2$ , the square of the inverse Debye screening length is  $q^2 = \frac{4\pi e^2}{\epsilon k_B T} (Z\rho + \sum Z_k \rho_k)$ ,  $\rho_k$  is the number density of the  $k^{th}$  species,  $Z$  is the valence of any added electrolyte, and  $\rho$  is the corresponding number density. Because of effective screening DLVO potential the DLVO potential is not as long ranged as the Coulomb potential. Thus, we did not find it necessary to use Ewald summation. Instead, we neglected, without loss of accuracy, interactions beyond a cut-off distance  $r_c$  determined by  $V_{ij}(r_c) = 0.001 k_B T$ . The parameters used in the simulations, listed in Table 1, correspond to the experimental system [23].

**Simulation Details.** We performed Brownian dynamics simulations (suitable for colloidal suspensions in water) by integrating the following equations of motion,

$$\frac{d\vec{r}_i(t)}{dt} = -\nabla_{\vec{r}_i} U(\vec{r}_1, \dots, \vec{r}_N) \frac{D_i}{k_B T} + \sqrt{2D_i} \vec{R}_i(t) \quad (2)$$

where  $\vec{r}_i(t)$  is the position of  $i^{th}$  particle,  $U(\vec{r}_1, \dots, \vec{r}_N)$  is  $\sum_{i \neq j} V_{ij}(r_{ij})$ ,  $D_i$  is the diffusion coefficient of the  $i^{th}$  particle,  $\vec{R}_i(t)$  is the random noise satisfying  $\langle \vec{R}_i(t) \cdot \vec{R}_j(t') \rangle = 6D_i \delta_{ij} \delta(t - t')$  with  $\delta_{ij}$  being the Kronecker delta and  $\delta(t - t')$  is the Dirac delta function. Because of computational considerations we neglected hydrodynamic interactions, whose effects we intend exploring in the future.

Since the quantities of interest in this study are the two-point density-density correlation function and the associated fluctuations (four point susceptibility) the integration step,  $\delta t$ , integration must be smaller than the characteristic time scale,  $a_s^2/D_1$ , in which the two-point density decays. The characteristic distance between particles is  $a_s = \rho^{-\frac{1}{3}}$  where  $\rho = \frac{(N_1 + N_2)}{V}$  with  $V$  being  $\rho$ -dependent size of the simulation box. The neglect of inertial effects is justified

if  $\delta t$  is larger than the characteristic decay time,  $m_1 D_1 / k_B T$  of the velocity correlation function. The values of  $D_k$  ( $k = 1$  or  $2$ ) are obtained using  $D_k = \frac{k_B T}{6\pi\eta a_k}$  where  $\eta = 0.89 \text{ mPa} \cdot \text{s}$  for water. With these values the range for  $\delta t$  turns out to be from 10 ns to 1 ms. We chose  $7\mu\text{s}$  for  $\delta t$  as a compromise between accuracy and computational costs. The use of real times is only for estimates, and they may not precisely correspond to experimental times.

The colloidal system is specified by  $\rho$  and temperature  $T$ , which we set to 298K. In contrast to the usual simulations of mixtures of soft spheres or Lennard-Jones particles in which glass formation is driven by quenching  $T$  it is  $\rho$  that controls Wigner glass formation [23]. We use the volume fraction,  $\phi = \frac{4\pi}{3V}(N_1 a_1^3 + N_2 a_2^3)$  as a measure of  $\rho$ . In most cases we measure distances in units of  $a_s = \rho^{\frac{1}{3}}$ . The 50:50 mixture used in our simulations corresponds to  $N_1 = N_2 = 5000$ .

We performed equilibration of the system of  $10^4$  particles by placing them initially at the sites of body-centered cubic lattice in a periodic simulation box. The size of box was adjusted to obtain the desired  $\phi$ , and it ranged from (2,500 - 5,000) nm ( $\approx (46 - 92)a_1$ ) depending on  $\phi$ . To achieve thermal equilibration, we carried out slow-quenching by controlling the concentration of electrolytes following the method used in [38]. The ratio of the concentration of electrolytes to colloids  $\bar{\rho} = \rho / Z^{-1} \sum_k Z_k \rho_k$  was initially set to 5, and the equations of motion were integrated for  $2 \times 10^5 \delta t$  in the liquid phase (low  $\phi$ ), and  $10^6 \delta t$  in a highly jammed glassy state (high  $\phi$ ). Subsequently, we reduced  $\bar{\rho}$  by half, and the simulations were further carried out with the reduced  $\bar{\rho}$ . This procedure was repeated until  $\bar{\rho}$  reached  $5/2^{10}$ . After reaching the final value,  $\bar{\rho}$  was set to zero. The protocol used here was needed to relax the system especially at high values of  $\phi$ . We performed the same process was for  $\phi=0.01, 0.02, 0.03, 0.04, 0.05, 0.075, 0.1, 0.125, 0.15, 0.175$  and  $0.2$ . After equilibration data were collected for  $10^5$  time steps. Since this time is not long enough to obtain structural relaxation dynamics for  $\phi \geq 0.075$ , we performed additional simulations for times ranging from  $10^6 \delta t$  to  $4 \times 10^6 \delta t$  when the system reached high density jammed state. For example, at  $\phi = 0.2$ , total simulation time was  $5 \times 10^6 \delta t$ , which still proves to be not long enough to accurately extract structural relaxation times at high  $\phi$  values. We generated 20 trajectories at each  $\phi$  and ensemble averages, where appropriate, were performed over the trajectories.

### III. RESULTS AND DISCUSSION

#### RADIAL DISTRIBUTION FUNCTIONS:

The radial distribution functions, and the associated structure factors for various volume fractions are shown in Fig. 1a. As has been established in many previous studies for a variety of systems the static pair functions,  $g_{11}(r)$ ,  $g_{12}(r)$ , and  $g_{22}(r)$  do not vary significantly except for some very minor changes in the first peak. In addition, there is clear evidence for split second peak, which is often found in glass forming systems [41]. The longer (compared to systems interacting with soft sphere and Lennard-Jones potential) range nature and strength of the interaction leads to short range order that persists for several values of  $a_s$  even at low volume fractions. For the highly charged micron-sized particles studied here the effective hard sphere diameter is considerably larger than the bare particle size [39, 42]. Thus, although technically these can be thought of as low-density low-density systems even the lowest value of  $\phi$  would correspond to a dense equivalent hard sphere liquid. Apart from this observation, it is worth reiterating that the pair functions show practically no change even as  $\phi$  is increased by twenty fold, hence carry no signature of the SGT.

#### DEPENDENCE OF DIFFUSION COEFFICIENTS ON $\phi$ :

The mean-square displacement (MSD) as a function of  $t$ ,

$$\langle \Delta r_\alpha^2(t) \rangle = \frac{1}{N_\alpha} \sum_{i=1}^{N_\alpha} \langle [r_i(t) - r_i(0)]^2 \rangle \quad (3)$$

with  $\alpha = 1$  (small sized particles) or 2 (large size particles) are shown in Figs 2A and 2B respectively. There are three regimes that are discernible. At short times  $t \leq \frac{a_s^2}{D_{\alpha 0}}$ , we find that  $\langle \Delta r_\alpha^2 \rangle$  increases linearly with  $t$  with a slope that is proportional to the short time diffusion constant,  $D_{\alpha 0}$ . As is well known this regime represents caging of a test particle by the neighbors. At longer times there is a plateau, whose duration increases as  $\phi$  increases. Finally, at much longer times the particles undergo diffusive motion, and  $\langle \Delta r_\alpha^2 \rangle$  again increases linearly now with  $D_\alpha$  being determined by interaction with particles.

The values of  $D_{\alpha 0}$ , obtained from the slopes of the initial increase in  $\langle \Delta r_\alpha^2(t) \rangle$  do not change significantly as  $\phi$  increases (Fig. 2C), because the extent of caging is only weakly dependent on



$\phi$ . However, the values of  $D_\alpha$ , calculated from the slopes of  $\langle \Delta r_\alpha^2(t) \rangle$  at long times (see Figs 2A and 2B), decreases rapidly as  $\phi$  increases (Fig. 2D), and nearly vanishes at  $\phi \sim 0.1$ , which is the first signature of the onset of glassy behavior. The values of  $D_\alpha$  for  $\alpha = 1$  and 2 are well fit using  $D_\alpha \approx (\frac{\phi_A}{\phi} - 1)^{\gamma_D}$ , where in analogy with the expectations based on RFOT we have identified  $T_A \sim \phi_A^{-1}$ . The fits, shown in Fig. 2E, yield  $\phi_A \approx 0.09$  and  $\gamma_D \approx (1.0 - 1.2)$  depending on the particle type  $\alpha$ . Three comments about these fits and the plateau duration (Fig. 2E) are worth making. (1) The values of  $\gamma_D$  are smaller than what is typically expected based on the mode coupling theory predictions. (2) We expect based on RFOT predictions [13, 19], and this is demonstrated below from an entirely different perspective, that  $\phi_A$  is the characteristic volume fraction at which there is an effective ergodic to non-ergodic transition. (3) The duration of the plateau in  $\langle \Delta r_\alpha^2 \rangle$  increases rapidly as  $\phi$  exceeds 0.09 (Fig. 2E) further indicating that this represents the dynamical transition density.

### **$\phi$ -DEPENDENCE OF RELAXATION OF DENSITY-DENSITY CORRELATION FUNCTION AND ACTIVATED TRANSPORT:**

The collective variable that slows down  $\phi > \phi_A$  is  $F_q(t)$ , the density-density correlation function defined as,

$$F_{\vec{q}}(t) = \frac{1}{N} \sum_{j=1}^N e^{i\vec{q} \cdot \vec{r}_j(t)} \sum_{k=1}^N e^{-i\vec{q} \cdot \vec{r}_k(0)} \quad (4)$$

where  $\vec{r}_i(t)$  is a position of  $i^{th}$  particle at time  $t$ . The ensemble-averaged isotropic self-intermediate scattering function  $\langle F_q(t) \rangle$  is estimated by integrating the ensemble averaged  $\langle F_{\vec{q}}(t) \rangle$ , with  $\langle \dots \rangle$  denoting ensemble average, over space with  $q = |\vec{q}|$ . The plots of the time dependence of  $\langle F_{\vec{q}}(t) \rangle$  for  $\phi = 0.01$  and  $0.02$  in Fig. 3A at  $q = q_{max} = \frac{2\pi}{r_s}$  (where  $r_s$  is the location of the first maximum in the total pair function calculated using both the particle types) show the usual vanishing of  $\langle F_{q_{max}}(t) \rangle$  in the liquid state at long times. In Fig. 3A the solid lines are fits of the simulation data to a stretched exponential function  $\langle F_{q_{max}}(t) \rangle \approx C \exp(-(\frac{t}{\tau_\alpha})^\beta)$  where the stretching exponent  $\beta \approx 0.6$  is fairly independent of  $\phi$ . In the inset to Fig. 3A we show the dependence of  $\langle F_{q_{max}}(t) \rangle$  for a range of  $\phi$ , with the corresponding stretched exponential fits with  $\beta \approx 0.6$ , which is identical to that found in experiments on hard sphere colloids [43]. When  $\phi$  exceeds about 0.15 the dynamics is so sluggish that  $\langle F_{q_{max}}(t) \rangle$  does not decay fast enough, which is an indication that there is a volume fraction,  $\phi_K \gg \phi_A$  at which the system undergoes

an ideal glass transition.

The dependence of  $\tau_\alpha$  on  $\phi$  is shown in the inset of Fig. 3A, with the line being the Vogel-Fulcher-Tamman (VTF) fit,

$$\tau_\alpha \approx \tau_{VTF} \exp\left[\frac{D}{\left(\frac{\phi_K}{\phi} - 1\right)}\right]. \quad (5)$$

By fitting  $\tau_\alpha$  to the VTF equation we obtain  $\tau_{VTF} = 0.01s$ , the fragility index  $D = 23$ ,  $\phi_K = 0.47$ . It is clear that the VTF also provides only a semi-quantitative fit of the entire data set. It appears to be a better description of the data at high  $\phi$ . However, the extremely slow dynamics at values of  $\phi$  far greater than  $\phi_A$  makes it difficult to obtain numerically converged results for  $\tau_\alpha$ . Nevertheless, given that  $\phi_K \gg \phi_A$  gives us confidence that there is a  $\phi \gg \phi_A$  at which the relaxation time associated with the Wigner glass essentially diverges. Because of numerical uncertainty associated with computing  $\tau_\alpha$  we cannot rule out the possibility that  $\delta$  associated with Eq.(5) can exceed unity as  $r = (\frac{\phi_K}{\phi} - 1)$  decreases from about 2, the highest  $\phi$  for which we can reliably compute  $\tau_\alpha$ .

### ERGODICITY BREAKING NEAR $\phi_A$ :

As has been emphasized previously the important feature at  $\phi_A$  ( $T_A$  in systems where temperature is the relevant variable) is that there is a break down in ergodicity, implying that time averages are no longer equivalent to ensemble averages. Of course, because the mosaic states are not truly disjoint ergodicity is only effectively broken, which implies  $\tau_{obs}$  is much less than  $\tau_\alpha$ . In order to determine whether such a transition occurs at  $\phi \approx \phi_A$  we calculated the energy metric, which is a general measure for assessing the necessary condition for establishing ergodic behavior in classical many body systems [22, 44]. The energy metric is obtained by first generating trajectories using two replicas (different initial conditions) of the system at the same volume fraction. For each replica we define the time average value of the energy of the  $i^{th}$  particle,

$$\bar{E}_\alpha^j(t) = t^{-1} \int_0^t E_\alpha^j(t') dt' \quad (6)$$

where  $E^j(s)$  is energy of particle  $j$  at time  $s$ , and  $\alpha$  labels the replica. The energy metric  $d_{\alpha\beta}(t)$  is defined as

$$d_{\alpha\beta}(t) = \sum_{k=1}^2 N_k^{-1} \sum_{i=1}^{N_k} \left[ \bar{E}_{\alpha;i}^k(t) - \bar{E}_{\beta;i}^k(t) \right]^2 \quad (7)$$

where  $N_k$  is the number of particles of type  $k$ ,  $\bar{E}_\alpha^j(t)$  and  $\bar{E}_\beta^j(t)$  are the energies of particle  $j$  in replica  $\alpha$  and  $\beta$  averaged over time  $t$ , respectively. If the system is ergodic on the observation time scale ( $\tau_{obs}$ ) then  $d_{\alpha\beta}(t)$  vanishes as  $t \rightarrow \tau_{obs}$ . Thus, when ergodicity is established we expect that  $\bar{E}_{\alpha;i}^k(\tau_\alpha) = \bar{E}_{\beta;i}^k(\tau_\alpha)$  independent of  $\alpha$  or  $\beta$  or  $i$ . This is the situation that pertains to the liquid phase. However, if ergodicity is broken, as is expected at  $\phi \approx \phi_A$ , then  $d_{\alpha\beta}(\tau_\alpha) \rightarrow C$  ( $C$  is a constant) suggesting that the two initial states do not mix on the time scale  $\tau_{obs}$ . As argued elsewhere [22], it is the development in time rather than any equal time correlation functions that distinguishes a glass from a liquid. It can be shown, using scaling-type arguments, that  $d_{\alpha\beta}(0)/d_{\alpha\beta}(t) \approx D_E t$  at long times where the ergodic diffusion constant  $D_E^{-1}$  sets the approximate time scale in which the two configurations ( $\alpha$  and  $\beta$ ) mix. Thus,  $Nd_{\alpha\beta}(0)/d_{\alpha\beta}(t)$  which is extensive in both  $N$  and  $\tau_{obs}$  in the liquid phase, remains only extensive in  $N$  in the glassy phase because  $\tau_\alpha \gg \tau_{obs}$ .

The energy metric as a function of  $t$  is shown in Fig. 4A from which it is clear that when  $\phi$  exceeds  $\approx 0.1$ , the values of  $d_{\alpha\beta}(t)$  essentially saturate indicating a break down of ergodicity. The reciprocal of the energy metric,  $d_{\alpha\beta}(0)/d_{\alpha\beta}(t)$  (Fig. 4B) clearly increases linearly with  $t$  at low densities and saturate as  $\phi$  increases at long times. From the linear dependence of  $d_{\alpha\beta}(0)/d_{\alpha\beta}(t)$  we calculated the dependence of  $D_E$  on  $\phi$  (Fig. 4C). We find that  $D_E \ll 1$  (nearly vanishes) at  $\phi \approx \phi_A$ , which implies that  $\phi_A$  is the volume fraction at which the time and ensemble averages start to deviate from each other [19]. The dependence of  $D_E$  on  $\phi$  can be fit using  $D_E \approx (\phi_A - \phi)^{\gamma_E}$  with  $\phi_A \approx 0.12$  and  $\gamma_E \approx 1.2$ . Remarkably,  $\phi_A$  extracted from the  $\phi$  dependence of  $D_E$  coincides with the value of  $\phi_A$  at which diffusion effectively ceases. Thus,  $\phi_A$  can be identified with the volume fraction at which ergodicity is broken.

#### FOUR POINT DYNAMICAL CORRELATION FUNCTION:

In order to distinguish between the liquid and glass-like states as  $\phi$  approaches  $\phi_A$  it is necessary to consider fluctuations in multi-particle correlation functions because there is no obvious symmetry breaking as the liquid becomes a glass. Sometime ago two of us [19] suggested that fluctuations in a suitably chosen order parameter describe the differences in the nature of states probed near  $\phi_A$  (or  $T_A$  when a liquid is cooled). The rationale for considering multi-particle correlation functions is that the natural order parameter that describes the onset of

SGT is the two particle  $F_q(t)$ , which decays to zero in the liquid phase, and saturates in the glassy phase at long times (Fig. 3). Thus, it is the only the fluctuations in  $F_q(t)$ , which plays the role of generalized susceptibility,  $\chi_4(q|t)$ , that can distinguish between the liquid and glassy states. Since we first showed  $\chi_{4|F_q}(t)$  (note the notation in [19] is different from the one used in subsequent development of this concept) can be used to describe genuine ergodicity breaking at  $T_A$  in mean field p-spin and Potts glasses a number of studies have used our measure (or some variants) to produce evidence for growing dynamical correlation length, and emergence of dynamic heterogeneity in a variety of model systems [21, 45–47].

The four point correlation function  $\chi_{4|F_q}$  is the ensemble averaged variance in  $F_q(t)$ , and is given by

$$\chi_{4|F_q}(t) = \langle F_q(t)^2 \rangle - \langle F_q(t) \rangle^2 \quad (8)$$

We calculated  $\chi_{4|F_q}(t)$  using a moving time averaging procedure in order to minimize numerical errors. We show plots of  $\chi_{4|F_q}(t)$  evaluated at  $q_{max}$  for various values of  $\phi$  in Fig. 5. As has been observed in a number of previous simulations on different systems the peak in  $\chi_4(t)$  increases as  $\phi$  increases. The dependence of the time,  $t^*$ , at which  $\chi_{4|F_q}(t^*)$  is a maximum is shown in the inset of Fig. 5. Although we are unable to compute  $\chi_{4|F_q}(t)$  accurately for  $\phi > 0.075$ , the changes in  $t^*$  as  $\phi$  changes can be fit to a power law. The details of the fit are in the caption to Fig. (5). It is noteworthy that  $\phi_A$  extracted from the fit is essentially the same as in the fit of  $D_E$  shown in Fig. 4C, thus establishing that the four-point susceptibility does probe the onset of ergodic - non-ergodic transition at  $\phi_A$ .

Although it is most natural to use fluctuations in  $F_q(t)$  to determine the four-point susceptibility others have considered different less obvious variables. One of these is the total overlap function,  $\Omega(\delta, t)$ , defined as [48],

$$\Omega(\delta, t) = N^{-1} \sum_{i=1}^N \omega(|\vec{r}_i(t) - \vec{r}_i(0)|, \delta) \quad (9)$$

where  $\vec{r}_i(t)$  is position of the  $i^{th}$  particle,  $N$  is number of particles, and  $\omega(x, \delta)$  is step function which is 1 when  $x \leq \delta$ .  $\Omega(\delta, t)$  depends on  $\delta$  and it is fixed at  $0.3a_s$ . The four-point function involving the fluctuations in  $\Omega(\delta, t)$  is defined as,

$$\chi_{4|\Omega}(t) = N \left[ \langle \Omega(t)^2 \rangle - \langle \Omega(t) \rangle^2 \right]. \quad (10)$$

In Fig. 6 we show the time evolution of  $\chi_{4|\Omega}(t)$  for various  $\phi$  values. Both  $\chi_{4|\Omega}(t)$  and  $\chi_{4|F_q}(t)$  evaluated at  $q_{max}$  are nearly identical. The dependence of  $t^*$  on  $\phi$  calculated using  $\chi_{4|\Omega}(t)$  also

shows a power law dependence (Fig. 6). The only difference is that the exponent characterizing the divergence of  $t^*$  as  $\phi \rightarrow \phi_A$  is 1.20 as opposed to 1.05 obtained in Fig. 5. It is gratifying that the two independent ways of computing four-point functions yield (nearly) quantitatively identical results. More significantly, the values of  $\phi_A$  as well as the exponents ( $\gamma_D$ ,  $\gamma_E$ , and  $\gamma_\chi$ ) characterizing the dependence of the translational diffusion coefficients, ergodic diffusion coefficient, and  $t^*$  are similar.

### **DYNAMICAL HETEROGENEITY IS A CONSEQUENCE OF VIOLATION OF LAW OF LARGE NUMBERS:**

A tenet of statistical mechanics is that many body systems obey the law of large numbers, implying that equilibrium properties of a large subsample is on an average identical to the entire sample. In the liquid phase ( $\phi < \phi_A$ ) the statistical properties of any subsample should coincide with that of the entire sample provided the subsample contains a large number of particles observation time is long enough compared to  $D_E^{-1}$ . In contrast, in the glassy phase we expect that statistical properties (distribution of energies of individual particles for example) of even a large subsample can deviate from that of the entire sample [22]. Moreover, one would expect that two distinct subsamples, which become equivalent in a liquid when viewed over a short period time, would remain inequivalent (or do not exchange) at volume fractions less than  $\phi_A$  even when  $\tau_{obs} D_E^{-1} \gg 1$ . Thus, no single subsample can characterize the distribution of observables of the entire sample in highly supercooled liquids. In other words, in the glassy phase the law of large numbers is violated, and there are subsample to subsample fluctuations. Only by examining the entire sample on time scale  $\tau_{obs} \gg \tau_\alpha$  can the equivalence of time and ensemble averages be established. These arguments suggest that the so called dynamical heterogeneity, which is one of the characteristic of glass forming systems [49, 50] is a consequence of the emergence of glassy clusters, which remain inequivalent even on  $t \gg \tau_{obs}$ . Because of the likely variations in both equilibrium and relaxation properties from subsample to subsample a glassy phase is inherently heterogeneous in a dynamical sense.

In order to illustrate the violation of large numbers we first consider an approximate measure of structural entropy  $s_3$  given by [51],

$$s_3 = \frac{\rho}{2} \int 4\pi r^2 [g(r) \ln g(r) - \{g(r) - 1\}] dr \quad (11)$$

where  $g(r)$  is pair-correlation function, and  $\rho$  is the number density. Parenthetically we note that the entropy density involves the full hierarchy of molecular distribution functions [51]. Here, we define a local structural entropy measure  $s_3^{(j)}$  for particle  $j$  using,

$$s_3^{(j)} = \frac{\rho}{2} \int 4\pi r^2 \left[ g^{(j)}(r) \ln g^{(j)}(r) - \{g^{(j)}(r) - 1\} \right] \quad (12)$$

where  $g_3^{(j)}(r)$  is pair-correlation with respect to the  $j^{th}$  particle. The time evolution of the distribution of  $P(\bar{s}_3|t_A)$  of the time-averaged  $\bar{s}_3$  (see below) for the entire sample and a subsample of size  $\xi \approx 3.3a_s$  (containing large enough particles) are used to demonstrate the violation of large numbers. The time-averaged local structural entropy associated with particle  $j$  is given by,

$$\bar{s}_3^j(t_A) = t_A^{-1} \int_0^{t_A} s_3^j(s) ds. \quad (13)$$

In Fig. 7A we show the distribution,  $P(\bar{s}_3|t_A)$  at different values of  $t_A$  for  $\phi = 0.02$ . As  $t_A$  increases  $P(\bar{s}_3|t_A)$  converges and its width narrows as expected for a system approaching equilibrium. In contrast,  $P(\bar{s}_3|t_A)$  for  $\phi = 0.2$  (Fig. 7B) is essentially frozen in time indicating that the transport of particles required for ergodicity to be reached does not occur on  $t_A = 12.5D_E^{-1}$ . It is more instructive to simultaneously compare the time evolutions of a large subsample and the whole sample for  $\phi = 0.02$  and  $\phi = 0.2$ . The four panels in Fig. 8 vividly show that for the liquid case ( $\phi = 0.02$ ) the distributions  $P(\bar{s}_3|t_A)$  are almost the same for all  $t_A$  values as is to be expected based on the law of large numbers. In contrast, at higher volume fractions ( $> \phi_A$ ) where ergodicity is effectively broken, the  $P(\bar{s}_3|t_A)$  for the subsample are substantially different from that of the entire sample, thus violating the law of large numbers. Interestingly, there are subsample to subsample variations in  $P(\bar{s}_3|t_A)$  even with  $t_A = 12.5D_E^{-1}$  as shown in the inset in Fig. 8D. Because different subsamples behave in a distinct manner and do not become equivalent the dynamics below is  $\phi_A$  is heterogeneous. Thus, emergence of dynamical heterogeneity is due to the violation of large numbers.

The inequivalence of particles in distinct regions has been probed by assessing how a subsample dynamically approaches the full sample using multi-dimensional NMR [52]. By measuring correlated rotational jump motions it was argued that time for exchanging between different subsamples indeed increases dramatically. While not conclusive, these experiments support the arguments relating violation of large numbers to dynamical heterogeneity.

Pictorially we can see how the frozen dynamics is manifested in Wigner glasses. In the top

panel in Fig. 9 we show the time evolution of particles within  $\xi \approx 3.3a_s$  for  $\phi = 0.02$ . It is clear that there are dramatic changes in the configuration, which explains how ergodicity is established by particles of a given type becoming equivalent on  $t \sim D_E^{-1}$ . It is worth noting that movement of these particles at  $\phi = 0.02$ , which is far above  $\phi_A$ , is highly correlated, and appear to undergo string-like motion. In sharp contrast, the particles at high density ( $\phi = 0.2$ ) are frozen. These represent low entropic droplets with considerable local order, which do not propagate across the entire sample. The emergence of local order, which is consistent with a number of recent studies on entirely different systems [35, 53] is inconsistent with string excitations at  $\phi(T)$  above (below)  $\phi_A$  ( $T_A$ ).

#### IV. CONCLUSIONS:

In this paper, we have used simulations of a binary mixture of charged colloidal liquid, which forms a Wigner glass, to confirm and relate many aspects of the RFOT of the STG transition. In most studies the SGT is studied by supercooling a liquid by varying temperature rather than controlling the density, which is the natural variable in colloidal suspensions. In particular, the simulations show that dynamics slows down before  $\phi_A$  is approached. Remarkably, three ways of measuring the time scale associated with dynamics (translational diffusion coefficient, ergodic diffusion constant, and the dramatic increase in the time at which the four point susceptibility has a maximum) all exhibit singular behavior at  $\phi \approx \phi_A$ . These results show that  $\phi_A$ , which should be identified with the mode coupling  $\phi_A$ , does represent the onset of breakdown of ergodicity, as predicted by considering by the dynamical aspects of  $p$ -spin and Potts glasses [11, 12, 19]. Although our goal is not to obtain precise values of the exponents  $\gamma_D, \gamma_E$ , and  $\gamma_\chi$  it is gratifying to note that they are approximately equal, which further underscores that the avoided dynamical transition density is physically relevant for the transition to the glassy state. It is worth stressing that MCT, which can be approximately related to equilibrium static density functional theory [54], does not provide a description of transport above (below)  $\phi_A$  ( $T_A$ ). Below  $\phi_A$ , the time scale for density relaxation increases dramatically, which is intimately connected to a growing correlation length [55–57]. In particular, the dependence of relaxation times is more consistent with the VTF law. The large value of  $r \approx (\frac{\phi_K}{\phi} - 1)$  prevents us from extracting the characteristic exponents that enter the description of transport based on the droplet picture

below  $\phi_A$  [1]. The value of  $\xi \approx 3.3a_s$ , with  $r \approx 1.4$ , is remarkably similar to the estimate made sometime ago for mixtures of Lennard-Jones particles [33]. The consistency of the data with VTF does suggest that the length scale,  $\xi$ , associated with the mosaic states must grow [35, 48, 57, 58] as the  $\phi$  (or  $T$ ) increases (or decreases) diverging near  $\phi_K$  or  $T_K$  with an exponent  $\nu = \frac{2}{3}$  in three dimensions. The value of  $\nu = \frac{2}{3}$  implies that the characteristic barrier height separating two mosaic states must scale as  $\Delta F^\ddagger \approx \xi^{\frac{d}{2}}$  [1]. Several simulations have confirmed our predictions [53, 59]. Our work further shows that the RFOT concepts [1] linking statics and dynamics [13], which have remained virtually unchanged since its introduction, is also valid for charged colloidal suspensions.

We conclude by briefly discussing the important features of RFOT, and comparing them to Adam-Gibbs theory of the glass transition that has a superficial resemblance to RFOT. The hallmarks of the RFOT theory of the structural glass transition are:

1. There is a temperature or density,  $T_A$  or  $\phi_A$ , where there is an avoided mean-field phase transition. Around this temperature there is a dramatic, power law singularity slowing down in the dynamics of the liquid. For  $T < T_A$ , or  $\phi > \phi_A$ , the transport involves transitions across free energy barriers, i.e., it is activated, hence the subscript  $A$ . The avoided transition temperature or  $\phi$  is identified with the mode-coupling glass transition temperature or  $\phi_A$ .
2. For  $T < T_A$  the driving force for the activated transport is a local complexity, which is similar to a configurational entropy,  $S_c$ , that vanishes at a lower temperature denoted by  $T_K$ . For  $T \rightarrow T_K^+$  the average relaxation time in the liquid is exponentially slow and is shown to be given by the VFT law. For  $T < T_K$  large scale transport ceases to occur.
3. As  $T \rightarrow T_K$  there is a length scale associated with the characteristic size of the glassy droplets,  $\xi$ , which are constantly transitioning from one metastable glassy state to another. This length diverges as  $\xi \sim (T - T_K)^{-2/d}$  according to very general arguments [1]. All three features are needed to understand numerous experimental and simulation results.

All three features, which require a unified treatment of the static and dynamical aspects of the SGT, are needed to understand numerous experimental and simulation results.

The RFOT theory of the SGT can be compared and contrasted to the Adams Gibbs theory. Most significantly, in the AG theory there is no such thing as a distinct  $T_A$ . The transport is



always activated, vanishing at a  $T_K$  where some sort of configurational entropy vanishes. The slow relaxation time is given by a VFT law. Therefore, it does not include the phenomena (ergodicity breaking and emergence of dynamic heterogeneity) associated with  $T_A$  or  $\phi_A$ , that are illustrated here using Wigner glasses as examples, and are generally associated with the MCT of the glass transition. Indeed, the absence of  $T_A$  or  $\phi_A$  in any theory of glasses should be considered a major weakness because numerous experiments clearly show that the very nature of transport changes at these temperatures or densities, perhaps in an universal manner [60]. Second, the AG characteristic length scale behaves as  $\xi \sim (T - T_K)^{-1/d}$  as  $T \rightarrow T_K$ . The  $\frac{1}{d}$  ( $\frac{1}{3}$  in three dimensions) exponent is not in agreement with simulation data [53, 59].

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TABLE I. Values of the number of particles ( $N_k$ ), electrostatic charge in units of  $e$  ( $Z_k$ ), radius ( $a_k$ ), mass ( $m_k$ ) and diffusion coefficient ( $D_k$ ) used in the simulations are presented. Here  $k$  refers to particle type. The values of  $D_k$  are computed using the Stokes-Einstein formula. All parameters are chosen to simulate the experimental system of Lindsay and Chaikin [23].

	$N_k$	$Z_k$	$a_k$	$m_k$	$D_k$
k=1	5000	300	545Å	$4.3 \times 10^8$ amu	$4.53 \mu\text{m}^2/\text{s}$
k=2	5000	600	1100Å	$34.4 \times 10^8$ amu	$2.24 \mu\text{m}^2/\text{s}$

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## Figure Captions

**Figure 1:** Pair correlation functions for binary charged colloidal particles.  $g_{11}(r)$  (A) Radial distribution functions,  $g_{11}(r)$ , between type-1 (smaller-sized) particles. The corresponding structure factors  $S_{11}(q)$  are in the inset. (B) Same as (A) except these curves are for the larger-sized particles. The inset contains  $S_{22}(q)$  plots. between type-2 particles, and  $g_{12}(r)$  (C) Pair functions between type-1 and type-2 particles and the corresponding  $S_{12}(q)$ . In all panels distance is measured in units of  $a_s$  and the scattering wave vector is in unit of  $\frac{2\pi}{a_s}$ . Volume fraction,  $\phi$ , presented here are 0.2, 0.175, 0.15, 0.125, 0.1, 0.075, 0.06, 0.05, 0.04, 0.03, 0.02 and 0.01 from top to bottom.

**Figure 2:** Mean-squared displacements (MSD) as a function of time,  $t$ . (A) Time-dependent changes in MSD,  $\langle \Delta r_1^2(t) \rangle$  as a function of type-1 particles. (B) Same as (A) except the plots correspond to  $\langle \Delta r_2^2(t) \rangle$ . In both (A) and (B) the  $\phi$  values are 0.01, 0.02, 0.03, 0.04, 0.05, 0.06, 0.075, 0.1, 0.125, 0.15, 0.175 and 0.2 from top to bottom. We have normalized,  $\langle \Delta_\alpha^2(t) \rangle$  by  $a_s^2$ . (C) Diffusion coefficient in the short time limit for type-1 particles (red squares) and type-2 particles (blue circles) as a function of  $\phi$ . (D) The values of the diffusion coefficients obtained from the long time values of  $\langle \Delta_\alpha^2(t) \rangle$  as a function of  $\phi$ . (E) Fits of diffusion coefficients in (D) to power-law  $\approx (\phi^{-1} - \phi_A^{-1})^{\gamma_D}$ . The fits yield  $\phi_A = 0.06$  for type-1 particles (red, filled square) and 0.064 for type-2 particles (blue, filled circle). The values of  $\gamma_D$  are 1.0 and 1.2 for type-1 and type-2 particles, respectively. (F) Length of plateau  $\ln(\tau_p)$  in (A) and (B) are plotted as a function  $\phi$ . Plateau length is defined by the region where  $\left| \frac{d \ln \Delta r^2}{d \ln t} \right|$  is less than 0.3.

**Figure 3:** Characteristics of the scattering function. (A) Self-intermediate scattering function  $F_q(t)$  at  $q = q_{\max}$  are presented for various  $\phi$ . To illustrate the goodness of the stretched exponential fits we show  $F_{q_{\max}}(t)$  at  $\phi=0.02$  (blue) and 0.01 (red). The relaxation times  $\tau_\alpha$  as a function of  $\phi$  are shown in the inset. The line, a fit to the VFT-law  $\tau_0 \exp \left[ \frac{D}{(\phi_A/\phi - 1)} \right]$  with the exclusion of  $\phi = 0.175$  and 0.2, gives  $\tau_0 = 0.01\text{sec}$ ,  $D = 22.7$  and  $\phi_K = 0.465$ . (B) The set of curves for the time-dependence of  $F_q(t)$  at  $q = q_{\max}$  corresponding to  $\phi = 0.2, 0.175, 0.15, 0.125, 0.1, 0.075, 0.06, 0.05, 0.04, 0.03, 0.02, 0.01$  from top to bottom are displayed. All the displayed  $F_q(t)$  at  $q = q_{\max}$  curves are fit to a stretched exponential function  $C \exp \left[ - (t/\tau_\alpha)^\beta \right]$  with  $\beta = 0.6$ . The quality of the fits justifies the assumption that  $\beta$  is a constant.

**Figure 4:** Probes of ergodicity breaking. (A) Energy metric,  $d_{\alpha\beta}(t)$  as a function of  $t$  for various  $\phi$ . The values of  $\phi$ s presented are 0.2, 0.175, 0.15, 0.125, 0.1, 0.075, 0.06, 0.05, 0.04,



0.03, 0.02 and 0.01 from top to bottom. (B) The reciprocal  $d(0)/d(t)$  plots are fit to  $D_E t + C_E$  to extract  $D_E$  (C) Dependence of  $D_E$  on  $\phi$  is plotted. The dependence of  $D_E$  on  $\phi$  can be fit using  $D_E \approx (\phi_A - \phi)^{\gamma_E}$  with  $\phi_a \approx 0.10$  and  $\gamma_E \approx 1.2$ . (D) The same data in log-log scale is used to illustrate the dramatic decrease in  $D_E$  as  $\phi$  approaches  $\phi_A$ .

**Figure 5:** Four-point susceptibility  $\chi_4(t)$  function determined by fluctuations of self-intermediate scattering function  $F_q(t)$  for all pairs of particles. We fix  $q$  is fixed at the first peak of total structure factor calculated irrespective of particle identity. We present results for  $\phi$  0.02, 0.03, 0.04, 0.05, 0.06 and 0.075 from left to right. The convergence at higher values of  $\phi$  are too slow to be reliable. In the inset the position of the peak  $t^*$  as a function is shown as solid squares. The solid line represents a power-law  $(\phi^{-1} - \phi_A^{-1})^{-\gamma_\chi}$  to the data. The fit gives  $\phi_A \approx 0.1$ , and is the MCT volume fraction for the Wigner glass. Note that this is the same value extracted by fitting the dependence of the diffusion coefficients and the ergodic diffusion coefficient on  $\phi$ . The value of the exponent  $\gamma_\chi$  is 1.05.

**Figure 6:** Evolution of four-point function  $\chi_{4|\Omega}(t)$  defined by variation of total overlap function  $\Omega(\delta, t)$  for all pairs of particles. We show  $\chi_{4|\Omega}(t)$  for  $\phi$  0.02, 0.03, 0.04, 0.05, 0.06 and 0.75 from left to right. Inset shows the dependence of the position of the peak  $t^*$  in  $\chi_{4|\Omega}(t)$  (squares). The solid line is a fit to a power-law  $(\phi^{-1} - \phi_A^{-1})^{-\gamma_\chi}$ . The fit gives  $\phi_A \approx 0.1$ . The value  $\gamma_\chi$  is 1.20.

**Figure 7 :** (A) Distribution of time-averaged  $\bar{s}_3$  for liquid ( $\phi = 0.02$ ) at various time intervals are plotted. Here, time interval  $t_A$  is 12.5, 7.5, 5, 2.5, 1.25, 1 and  $0.5D_E^{-1}$  from top to bottom. (B) The same graph for glass ( $\phi = 0.02$ ) with the same time interval as in (A).

**Figure 8 :** Dependence of  $P(\bar{s}_3|t_A)$  for different values of  $t_A$ . (A) The red and green curves correspond to the entire sample and a subsample with size  $\xi \approx 3.3a_s$ , respectively. The volume fraction is  $\phi = 0.02$ . The blue curve gives  $P(\bar{s}_3|t_A)$  for a subsample of a glassy state, and the black is the corresponding result for the entire simulation box. The value of  $t_A = 0.5D_E^{-1}$ . (B-D) same as (A) except the values of  $t_A$  change as indicated. In the inset in (D) we also show  $P(\bar{s}_3|t_A)$  for another subsample in red. The structural features of the two subsamples are shown in Fig. 9.

**Figure 9 :** Illustration of time evolution of particles within  $\xi = 3.3a_s$ . The panels on top are for a liquid ( $\phi = 0.02$ ) at two times ( $t = 0$  and  $t = 2D_E^{-1}$ ). Small particles are colored in yellow and large particles are in violet. An unmistakable correlated string-like motion is evident

especially for the motion of the large particles. The bottom panels show how two different subsamples at  $\phi = 0.2$ , whose  $P(\bar{s}_3 I(t_A))$  for  $t_A = 12.5 D_E^{-1}$  are shown in the inset in Fig. 8D, evolve over time. Blue spheres represent small particles and red corresponds to large particles. While snapshot shows large difference between (left, top) liquid at initial time and (right top) at  $t = 2 D_E^{-1}$ , particles are frozen in glassy state thus there is little change between  $t = 0$  (left, bottom) and  $t = 2 D_E^{-1}$  (right, bottom) for glass. Most importantly, there are no string-like excitations below  $\phi_A$ . Instead, the snapshots show clear evidence for local order [53].